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Hydroxide-ion-conductive, gas barrier films based on layered double hydroxide/polysulfone multilayers

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Experimental details

Materials

Polysulfone (PSF) was purchased from Sigma-Aldrich. $Co(NO_3)_2•6H_2O$, $Al(NO_3)_3•9H_2O$, chlorotrimethylsilane, paraformaldehyde, anhydrous tin chloride ($SnCl_4$), trimethylamine and formamide were obtained from Aladdin. Co. Ltd. The other chemicals, including NaOH, urea, chloroform, N,N-dimethylformamide, ethanol and acetone were purchased from Beijing Yili Co. Ltd.

Synthesis of CoAl-LDH nanoplates

CoAl-LDH nanoplates were synthesized *via* a facile co-precipitation method, including separated nucleation and aging steps, as previously reported by our group.[1] Firstly, 100 ml solution composed by $Co(NO_3)_2•6H_2O$ (0.20 M) and $Al(NO_3)_3•9H_2O$ (0.10 M) were simultaneously added to a colloid mill with 400 ml NaOH (0.15 M) solution. The speed of the colloid mill was controlled as 3000 rpm; and the mixing time is 1 min to obtain slurry of CoAl-LDH. The resulting LDH slurry was placed in a stainless steel autoclave with a Teflon lining and heated at 110 °C for 24 h. After the hydrothermal treatment, CoAl LDH wet cake (solid content: ~15%) was obtained *via* washing several times and centrifuging. The LDH colloidal suspensions with various concentrations (0.2%, 0.5%, 0.8% and 1.0%) were prepared by dispersing different weights of wet cake into deionized water.

Chloromethylation and quaternization of PSF to prepare QAPSF

The QAPSF was synthesized following a two-step procedure,[2] including sequential chloromethylation and quaternization of PSF. The specific details for each step are as follows.

Chloromethylation of PSF. Chlorotrimethylsilane (42.5 mL) and paraformaldehyde (10.0 g) were added to a round-bottom flask containing a PSF solution (14.88 g in 750 mL chloroform). The reaction flask was fitted with a reflux condenser and heated to 50 °C. After mixing for 40 minutes, 0.39 mL anhydrous tin chloride was added dropwise to the reaction solution. Then the mixture was stirred for 24−48 with, depending on the desired chloromethylation degree (DCM). Upon completion, the reaction solution was washed with excess ethanol and dried in a vacuum desiccator at 60 °C for 24 hours to yield chloromethylated polysulfone (CMPSF) in white powder form.

Quaternization of CMPSF. QAPSF was synthesized by *in situ* quaternization of CMPSF. Specifically, 1 g CMPSF was dissolved into 10 ml N, N-dimethylformamide, and then 2 mL trimethylamine was added dropwise to the reaction solution. After stirring under ambient conditions for 48 hours, the QAPSF was obtained.

Fabrication of (LDH/QAPSF)$_n$ multilayer films

The LDH nanoplates and QAPSF was used as building block to fabricate (LDH/QAPSF)$_n$ films by a layer-by-layer (LBL) deposition technique. The quartz glass and poly(ether ether ketone) (PEEK) films were employed as substrates for various characterizations: PEEK substrate was used for gas barrier, ion conductivity, thermogravimetry and stress-strain measurements; quartz glass was utilized for other analysis (including XRD, SEM, AFM, UV-vis, etc). The cleaned substrate was firstly dipped in the colloidal suspension of LDH nanoplates for 10 min followed by washing thoroughly. Then the pre-coated substrate was immersed into QAPSF solution (10 wt%) for another 10 min followed by washing thoroughly. The (LDH/QAPSF)$_n$ multilayer films were obtained by cycling such operation for *n* times.

Sample Characterizations

X-ray diffraction (XRD) patterns for the LDH powder and (LDH/QAPSF)$_n$ films were recorded by a Rigaku XRD-6000 diffractometer, using Cu Kα radiation (λ = 0.1542 nm) at 40 kV, 30 mA. The morphology was investigated using a scanning electron microscope (SEM; Zeiss SUPRA 55) with the accelerating voltage of 20 KV. The Fourier transform infrared (FT-IR) spectra were obtained using a Vector 22 (Bruker) spectrophotometer with 2 cm^{-1} resolution. The ^{1}H NMR measurements were performed on a Varian Mercury 600 MHz FT-NMR using deuterated dimethyl sulfoxide (DMSO) solvent. The UV-vis absorption spectra were collected in the range 200−800 nm on a Shimadzu U-3000 spectrophotometer. A NanoScope IIIa atomic force microscope (AFM) from Veeco Instruments was applied in analyzing the roughness of the film. Loading of LDH in the films was measured by inductively coupled plasma (ICP) emission spectroscopy (Shimadzu ICPS-7500). X-ray photoelectron spectra (XPS) were recorded on a Thermo VG Escalab 250 X-ray photoelectron spectrometer at a pressure of about 2×10^{-9} Pa with Al 193 Kα X-rays as the excitation source. Thermogravimetry analysis (TGA) was performed on a Beifen PCT-IA instrument at a heating rate of 5 °C/min in air. The gas barrier performance of (LDH/QAPSF)$_n$ films was evaluated by measuring the oxygen and hydrogen transmission rates (OTR and HTR) based on the differential pressure method, by using VAC-V2 gas transmission rate testing equipment from the Labthink Instrument Co., Ltd. Oxygen and hydrogen were selected as the probe molecules, because they are the main raw materials of a hydrogen/oxygen fuel cell, which should be rigorously separated and prohibited to diffuse across the electrolyte membrane. All the OTR and HTR values were averaged from at least three separate films.

Chloromethylation degree (DCM) was determined on basis of the change in molecular weight of PSF before and after chloromethylation, following these two formulas:

$$M_{\mathrm{W}} = 442\ m/m_0$$

$$\mathrm{DCM} = (M_{\mathrm{W}} - 440)/49.5$$

where M_{W} represents the molecular weight of the CMPSF; m and m_0 are the mass of CMPSF and PSF; 442 is the molecular weight of PSF repeat unit; 440 is the molecular weight of PSF repeat unit subtracting two hydrogen atoms on the phenyl ring; 49.5 is the molecular weight of chloromethyl group ($-CH_2Cl$).

Two-probe alternating current (AC) impedance method is an effective technique to measure the ion conductivity of film materials. Electrochemical impedance spectra (EIS) measurements were performed by the two-probe AC impedance method over the frequency range of 0.01 to 100 kHz on an electrochemical workstation (CHI 660C) at room temperature. Before measurement, the films were immersed into 1 mol L^{-1} sodium hydroxide solution for 48 h. Then, the films were washed by abundant water until the pH of residual water was neutral. Chemical stability of the $(\mathrm{LDH/QAPSF})_n$ films was investigated by measuring hydroxide conductivity after exposure of the film to 1 mol L^{-1} KOH aqueous solution at 60 °C for different times. The membranes were then washed with deionized water to remove the residue KOH and their hydroxide conductivity was measured at room temperature. The ionic conductivity (σ) was calculated as follow:

$$\sigma = \frac{l}{AR_m}$$

where l is the distance between the two electrodes (cm), A is the cross-sectional area of the test membrane (cm^2), and R_m is the membrane resistance (Ω) acquired from a Nyquist plot.

Supplementary figures

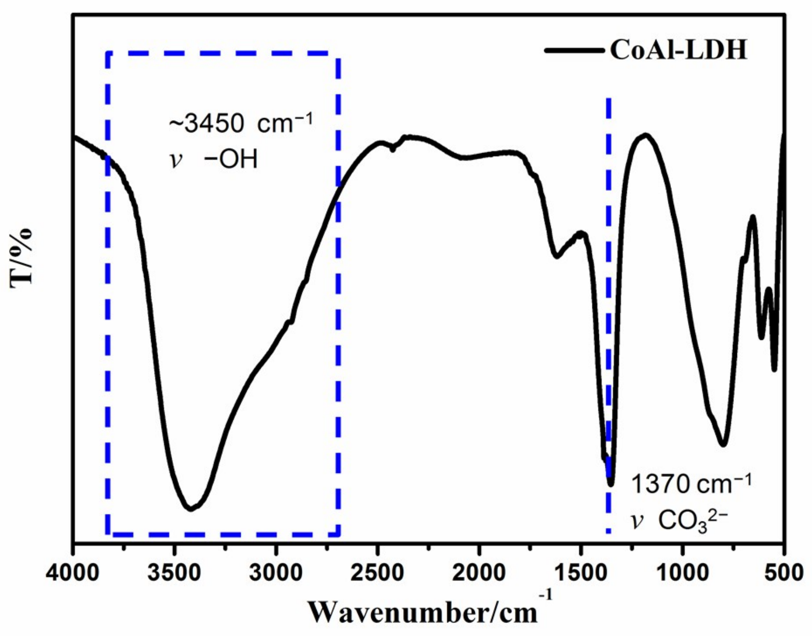

Fig. S1 FT-IR spectrum of the CoAl-LDH nanoplates.

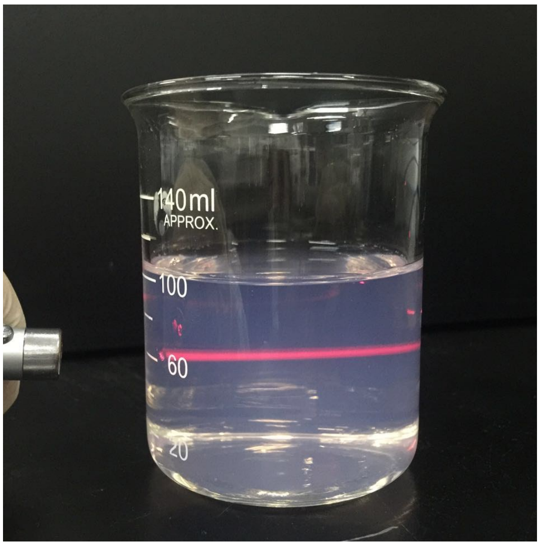

Fig. S2 The CoAl-LDH colloidal dispersion (0.2%) shows an obvious Tyndall effect under a laser.

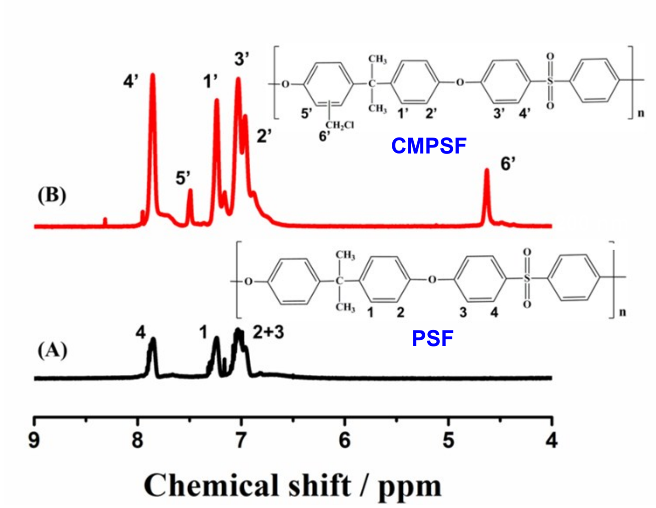

Fig. S3 NMR spectra of (A) PSF and (B) CMPSF.

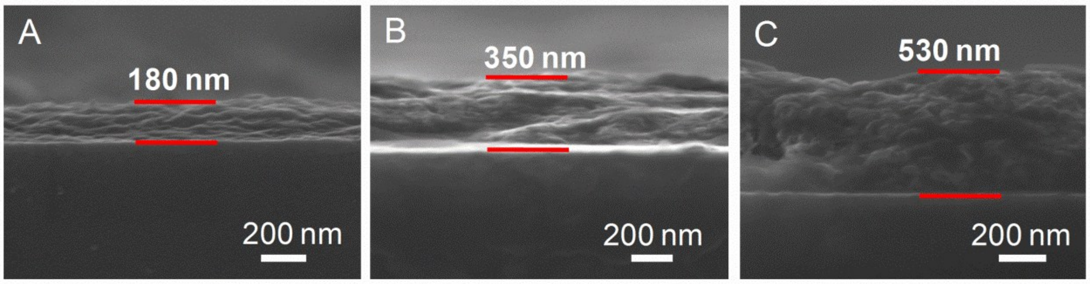

Fig. S4 Cross-view SEM images of the (LDH/QAPSF)$_n$ films with n = (A) 5, (B)10 and (C) 15.

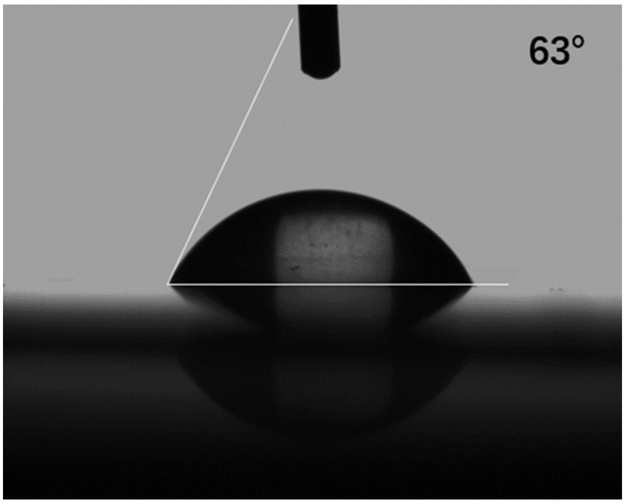

Fig. S5 Water contact angle of the (LDH/QAPSF)$_{15}$ film.

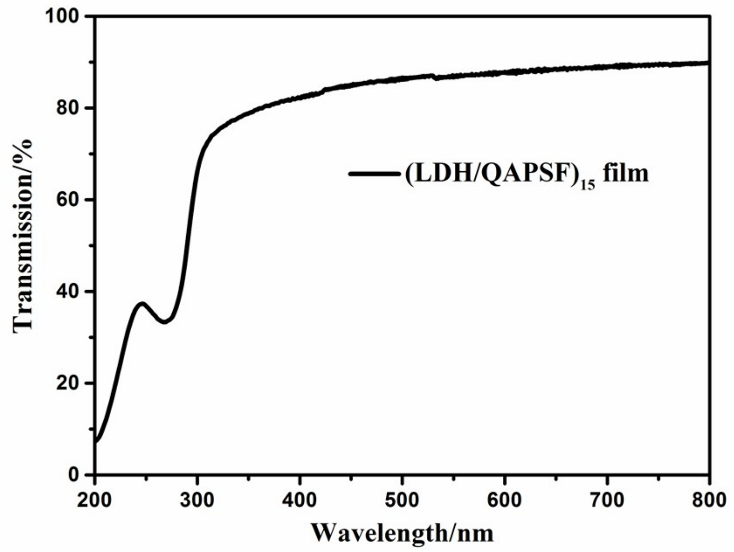

Fig. S6 The light transmittance of (LDH/QAPSF)$_{15}$ film.

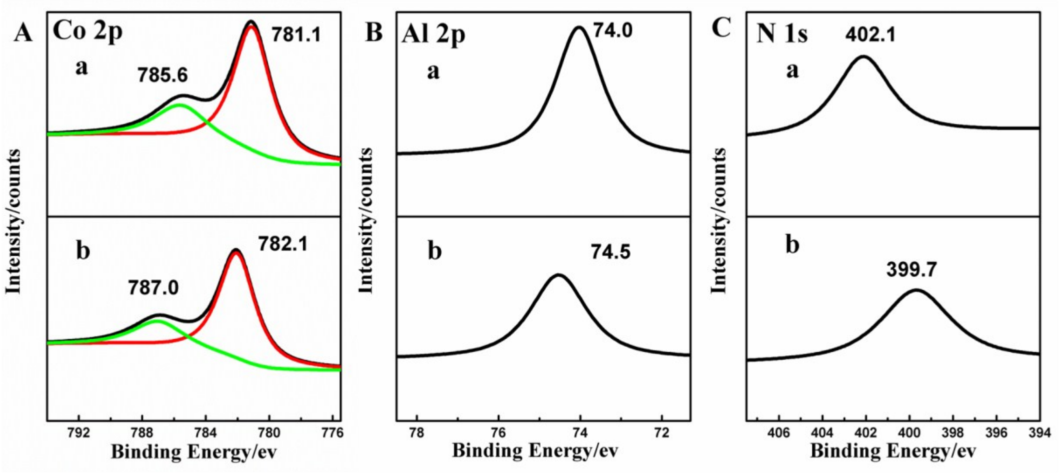

Fig. S7 (A) Co 2p, (B) Al 2p XPS spectra for (a) LDH and (b) (LDH/QAPSF)$_{15}$ film, (C) N 1s XPS spectra for (a) QAPSF and (b) (LDH/QAPSF)$_{15}$ film.

To investigate the interaction between LDH nanoplates and QAPSF, X-ray photoelectron spectroscopy (XPS) was performed on LDH, QAPSF and (LDH/QAPSF)$_n$ films (Fig. S7). For the precursor LDH, binding energies of Co 2p locate at 781.1 and 785.6 eV, corresponding to the Co^{2+} species in CoAl LDH. After assembly with QAPSF, they shift to 782.1 and 787.0 eV, respectively. Similarly, those of Al 2p shift to a higher energy as well, indicating the increase of oxidation state for the Co and Al elements. In addition, for the polymer QAPSF, the binding energy of N 1s (402.1 eV) reduces to 399.7 eV after assembly with LDH. These results suggest the formation of hydrogen bonds between –OH in CoAl-LDH and O=S=O groups in QAPSF.

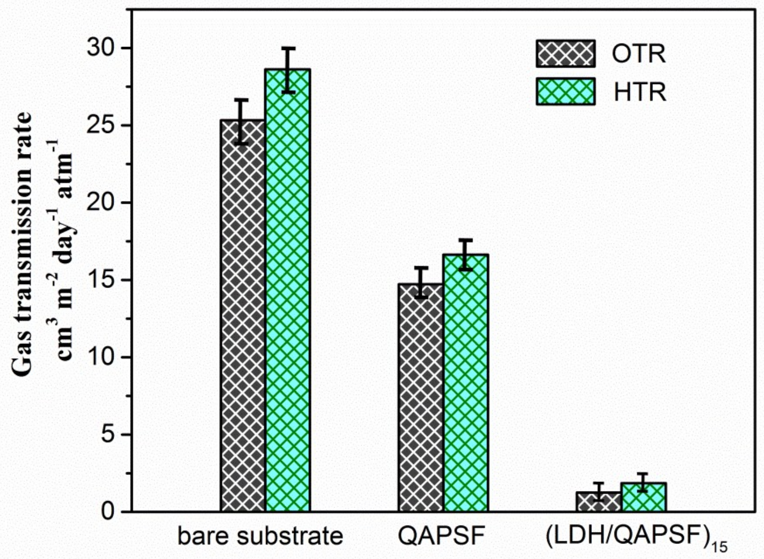

Fig. S8 OTR and HTR values for bare PEEK substrate, pure QAPSF and $(LDH/QAPSF)_{15}$ films. The thickness of pure QAPSF and $(LDH/QAPSF)_{15}$ film is almost the same (~530 nm).

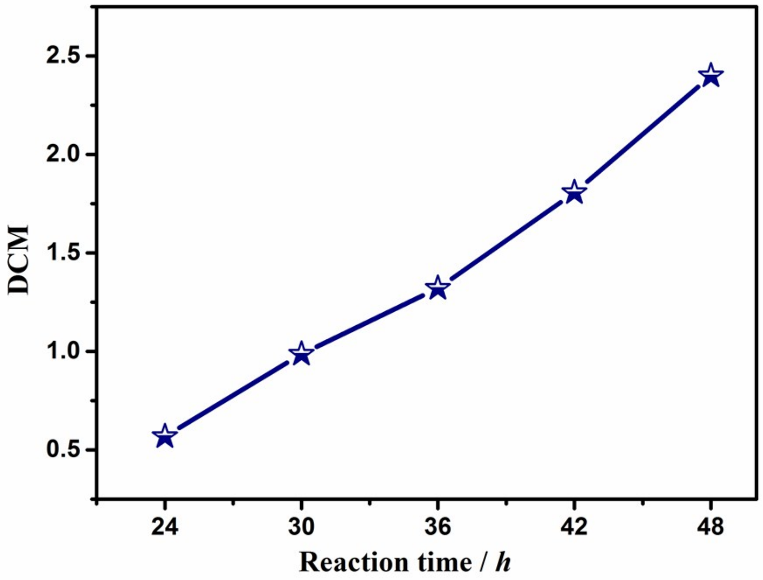

Fig. S9 The relationship between the DCM of PSF and chloromethylation time.

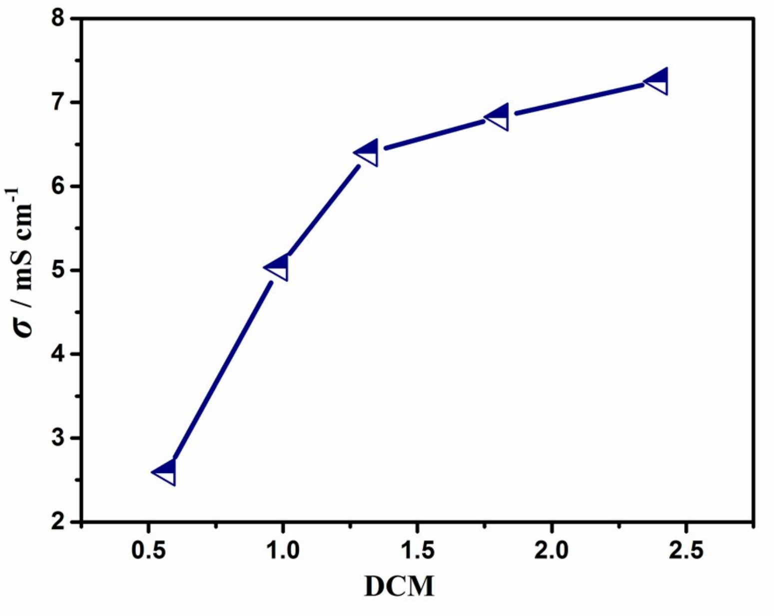

Fig. S10 Ionic conductivity of $(LDH/QAPSF)_{15}$ film as a function of DCM.

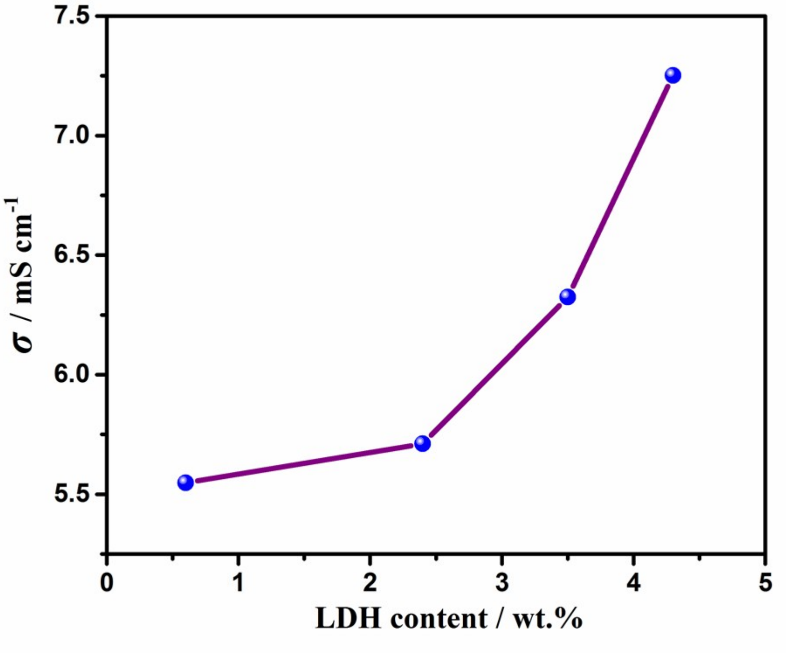

Fig. S11 Ionic conductivity of $(LDH/QAPSF)_{15}$ film as a function of LDH weight loading in the hybrids.

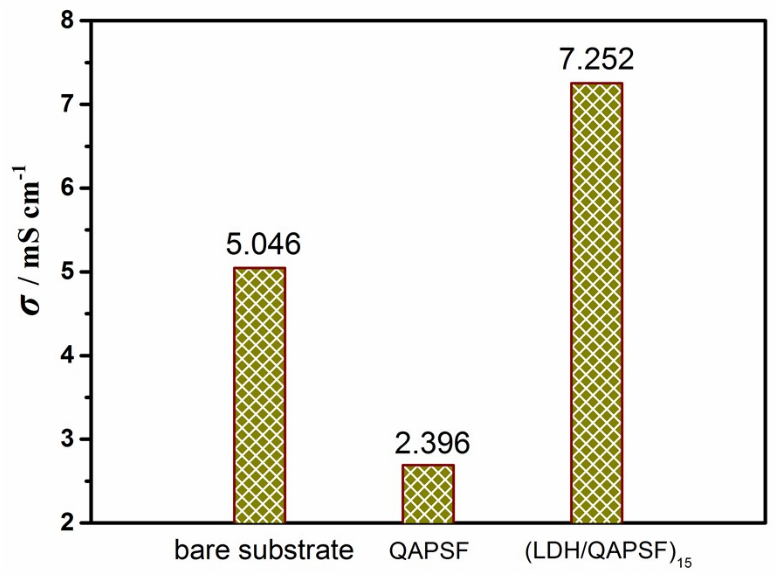

Fig. S12 Ionic conductivity of PEEK substrate, QAPSF and (LDH/QAPSF)$_{15}$ films. The thickness of pure QSPSF and (LDH/QAPSF)$_{15}$ film is almost the same (~530 nm).

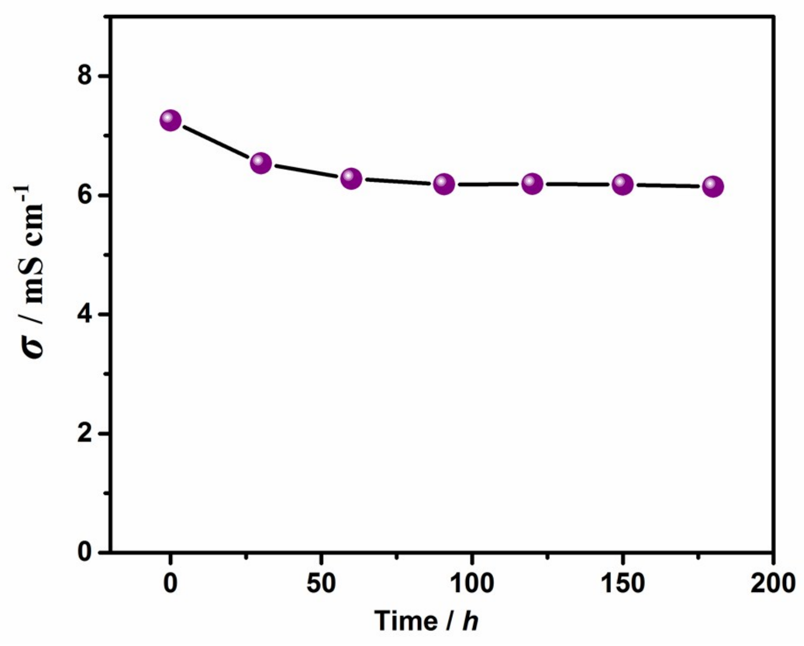

Fig. S13 Hydroxide ion conductivity of the (LDH/QAPSF)$_{15}$ film after exposure to 1 mol L^{-1} KOH aqueous solution at 60 °C for different times.

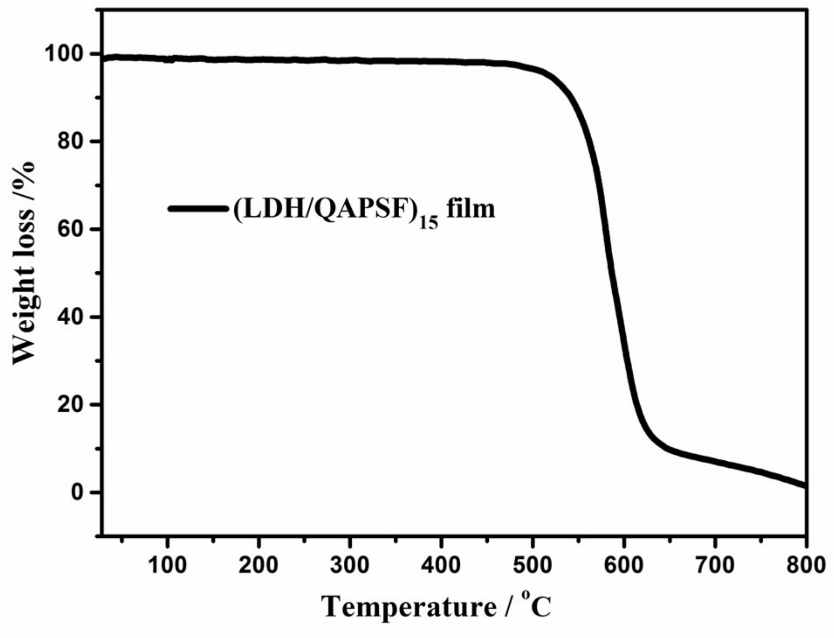

Fig. S14 Thermogravimetric curve for $(LDH/QAPSF)_{15}$ film.

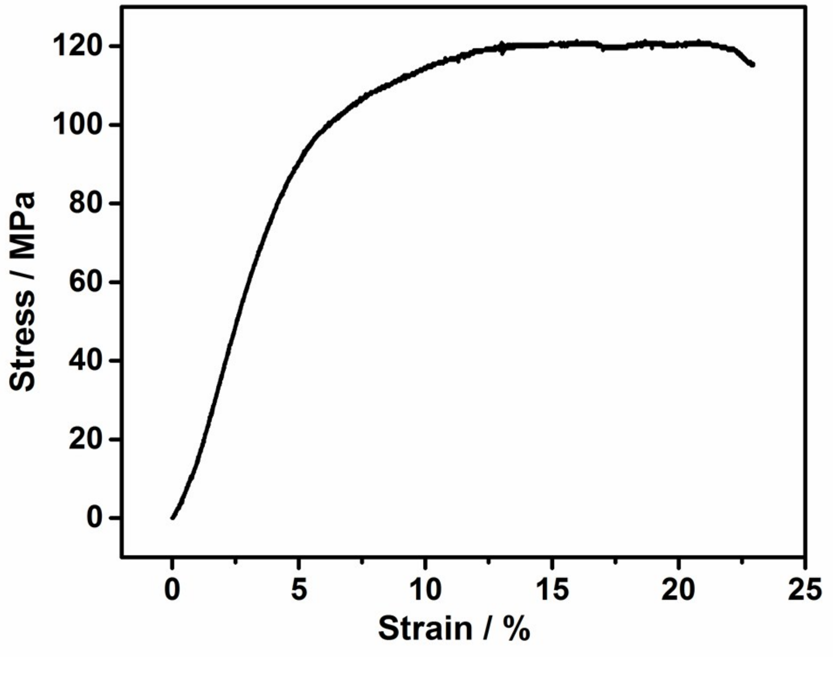

Fig. S15 The stress-strain curve of $(LDH/QAPSF)_{15}$ film.

References:

1. Y. Dou, T. Pan, S. Xu, H. Yan, J. Han, M. Wei, D. G. Evans and X. Duan, *Angew. Chem. Int. Ed.*, 2015, **54**, 9673−9678.
2. W. Shi, H. Li, R. Zhou, H. Zhang and Q. Du, *Bioresource Technol.*, 2016, **210**, 43−48.